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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US90/01154 <b>(22) International Filing Date:</b> 1 March 1990 (01.03.90)  <b>(30) Priority data:</b> 51496/89                      3 March 1989 (03.03.89)                      JP 53372/89                      6 March 1989 (06.03.89)                      JP 56593/89                      7 March 1989 (07.03.89)                      JP  <b>(71) Applicants:</b> JAPAN SYNTHETIC RUBBER COMPANY, LTD. [JP/JP]; 24, 11 ban 2-chome, Tsukiji, Chuo-ku, Tokyo (JP). HYPERION CATALYSIS INTERNATIONAL [US/US]; 128 Spring Street, Lexington, MA 02173 (US).  <b>(72) Inventors:</b> YONEKAWA, Yoshiaki ; HIRAHARU, Mitouo ; WATABE, Yasuhisa ; KATO, Minoru ; UMEDA, Itsuki ; SAKAI, Masato ; TANAKA, Tadaaki ; CHIKATSU, Yoshishige ; SAITO, Toshimi ; FURUTA, Isao ; Japan Synthetic Rubber Co., Ltd., 24, 11 ban 2-chome, Tsukiji, Chuo-ku, Tokyo (JP).		<b>(74) Agent:</b> FRENCH, Timothy, A.; Fish & Richardson, One Financial Center, Suite 2500, Boston, MA 02111-2658 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> APPLICATIONS FOR GRAPHITE FIBRILS  <b>(57) Abstract</b>  Compounds for carpet lining materials, rubber compounds, and electroconductive rubber compounds all containing graphite fibrils having diameters between 3.5 and 70 nm and lengths at least 5 times the diameter.		

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## APPLICATIONS FOR GRAPHITE FIBRILS

Background of the Invention

In a first aspect, this invention is related to a compound for carpet lining materials with low static.

5 Many of the recent problems in operating electronics equipment such as computers are caused by the static generated on carpets. Presently, methods such as addition of anti-static material in the lining compound or addition of electrically conductive fibers  
10 in the carpet pile have been available for manufacturing static-free carpets.

The carpet lining compounds based on the former method are manufactured by adding inorganic fillers, dispersants as needed, anti-aging agents, antifoams,  
15 bridging agents, etc., to a co-polymer latex, as well as anti-static agents such as carbon black, alkylester salt, nonionic surfactant, amphoteric surfactant, cationic quadrivalent ammonium salt, etc. prior to the final adjustment of viscosity to a desirable level by  
20 adding viscosity increasing agents. The desired properties for a carpet lining compound are low static in the carpet lined with the lining compound, easy handling during the manufacturing process, high stability of the viscosity, and high bonding strength  
25 between the main fabric and the secondary base fabric, all of which are not satisfactory at present and require improvements.

In contrast, the method for reducing the static in the carpet pile is done by adhering cellulose fibers, metal fibers, or carbon fibers to nylon, acryl, or  
30 polyester fibers during the polymer formation, spinning, or dying stage. However, further improvements in electro-static characteristics are desired.

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The inventors of this invention discovered that a carpet lining compound with low static could be manufactured by adding graphite fibril in a conventional carpet lining compound, hence achieving this invention.

5 In a second aspect, this invention relates to an electroconductive rubber compound which gives stable conductivity. More specifically, it relates to an electroconductive rubber compound manufactured by the addition of fine carbon fibrils and a special silane  
10 coupling agent into a rubber-like polymer.

Electroconductive rubbers have been used for the manufacturing of rolls, belts, tubes, hoses, and floor materials which require anti-static characteristics, power wires, semi-conductive layers of  
15 cables, and grounding wires.

Since organic polymers generally possess electrically insulating characteristics, addition of electrically conductive components such as metal powder, carbon or metal fibers, and ferrite are added in order  
20 to achieve electroconductivity.

In the case of rubbers, carbon black is normally used because the use of metal powders makes the achievement of mechanical strength more difficult.

However, a large amount of carbon black is  
25 required in order to obtain satisfactory conductivity if only carbon black mainly intended for reinforcement is added, which results in increased rubber hardness and poor workability which makes the compound impractical in some cases. In addition, resilience after vulcanization  
30 which is specific to the rubber is drastically decreased, resulting in poor elongation and high hardness.

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For the purpose of obtaining electroconductivity, special electrically conductive carbon black such as Ketchen Black, Vulcan XC72, acetylene black, etc. are available on the market, which  
5 make it possible to give high conductivity with a relatively small addition rate as compared to carbon blacks intended for reinforcement. However, these special carbon blacks have the disadvantage that they need special compounding and mixing technologies because  
10 they are more difficult to be dispersed into rubber, and the conductivity of the rubber compound is strongly dependent on the dispersion.

Furthermore, increase in the hardness becomes extremely large even with a small addition rate  
15 depending on the type of rubber, restricting the addition rate below certain level in the kneading process.

Although the use of carbon fibers is also an effective means for attaining electroconductivity, the  
20 fibers available on the market have relatively large diameters such as about 5-10 microns, and therefore they not only reduce the strength of the rubber but also create problems such as directional variation in strength associated with the fiber orientation, and  
25 insufficient conductivity.

Although the use of fine carbon fibers is very effective since it makes it possible to obtain high electroconductivity with a small amount of addition, the  
dispersion into rubber is not sufficient as it is also  
30 the case with carbon blacks available on the market, and also a long kneading time is required.

In the method of adding electroconductivity to a rubber compound, this invention aims at obtaining stable and high electroconductivity without losing the  
35 workability of the rubber compound.

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In a third aspect, this invention relates to a new rubber compound which has superior breaking strength, abrasion resistance, thermal deterioration resistance, and heat generation characteristics. More specifically, it is related to a rubber compound with superior hardness, workability, and breaking strength characteristics obtained by the addition of a small amount of special carbon fibril, and it further relates to a rubber compound suitable for tire tread obtained by the addition of a combination of the aforementioned special carbon fibril and carbon black into natural rubber, and it also relates to a rubber compound suitable for an oil-seal compound obtained by the addition of the aforementioned special carbon fibril into an oil resistant rubber.

High-hardness rubber compounds have been widely used not only in vehicle applications such as automobile parts and tires but also in general industrial applications such as rubber rolls, rolling, padding, etc., and their demands are rapidly increasing in recent years. Specification requirements for such rubbers are also becoming more stringent, and superior stability of the characteristics over a long period of time is required with particular importance.

Conventionally, high-hardness rubbers are obtained by adding a large amount of filler such as carbon black or white carbon, while reducing the mixing ratio for oils such as extending oil and plasticizer. Further, the concentration of bridge-network in the rubber is increased in order to obtain high-hardness rubbers. Therefore, it is essential to use vulcanization type compounds, particularly with a high sulfur content.



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Improvements in performances of tire treads used for large vehicles such as trucks and buses, particularly for radial-tire treads for trucks and buses (abbreviated as TBR tread hereinafter) have become  
5 urgently demanded in recent years due to the increasing vehicle weight and traveling speed. Particularly, improvements in abrasion resistance and reduction heat generation under high-load and high-speed conditions, and improvements in breaking strength and tear strength,  
10 which would prevent groove cutting caused by deeper tire grooves introduced for improving maneuverability under a high traveling speed, are urgently required.

Materials for the TBR tread have been manufactured by adding high-performance carbon black  
15 which is particularly effective in improving abrasion resistance, to natural rubber which has superior breaking and tear strengths and low heat generation. Such compounds manufactured by conventional methods more or less satisfied the requirements for the TBR tread in  
20 the past. However, the development of a new compound capable of meeting the more severe requirements created by the recent high-load and high-speed conditions is urgently needed.

In the manufacturing of a rubber compound for  
25 oil-seal application, solid lubricants such as graphite, molybdenum sulfide, polytetra-fluoroethylene, etc. are normally added to the compound in order to reduce the friction resistance between the lip and the shaft. However, these lubricants generally have poor affinity  
30 to rubber, and they do not have reinforcing effects resulting in undesirable physical strength characteristics. Furthermore, the addition of a greater amount of the reinforcing filler to meet the high hardness required for an oil-seal would further reduce  
35 the physical strength. Therefore, development of a new material is needed in this application as well.

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Although high-hardness rubber compounds can be obtained by conventional methods, the workability of such compounds is extremely poor because of the relatively high filler content and the relatively low oil content. In addition, the rubber elasticity is also lost because of the low rubber content in the compound, which in turn results in a reduction in the breaking strength and the abrasion resistance, and in increased heat generation. Furthermore, the addition of a large amount of sulfur inevitably decreases the thermal deterioration resistance. Therefore, rubber products obtained by conventional methods have shortcomings such as high manufacturing costs caused by the poor workability, and relatively short product life. Solutions to these shortcomings are urgently required.

The natural rubber used as the main component for the TBR tread has excellent characteristics such as high breaking and tear strengths which are considered to be the result of the elongation-crystallization phenomenon specific to natural rubber. The elongation-crystallization decreases with the addition of carbon black, the degree of decrease becoming greater as the reinforcing strength of the carbon black or its addition rate increases. Further, carbon black with a high reinforcing strength has a tendency to increase heat generation of the rubber when its addition rate is increased. However, a reduced addition of the carbon black not only gives insufficient abrasion resistance but also stops the elongation-crystallization. In addition, the stress at less than 300% elongation becomes low. It is also difficult to obtain a hardness sufficiently high for the treads. In summary, it was impossible by the conventional method to obtain the proper balance between abrasion resistance, low heat

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generation, tear strength, and breaking strength, which is required in the modern TBR treads. Therefore, development of a new compound suitable for the TBR tread has been asked for.

5 In order to solve the aforementioned problems of the TBR tread compounds, it was necessary to discover an alternative compounding material to replace carbon black so that the elongation-crystallization phenomenon at a high elongation specific to the natural rubber used  
10 as the base material could be maintained, while maintaining the elongation stress and the hardness at low elongation and the superior abrasion resistance.

In oil-seal applications, the friction resistance of the rubber surface must be reduced while  
15 the mechanical strengths are maintained.

#### Detailed Description of the Invention

##### A. Carpet Lining Compounds

The carpet lining compounds manufactured by this invention contain 0.5-20 weight % of graphite  
20 fibril, whose diameter is 3.5-70 nm and its length is at least 5 times the diameter, against 100 weight parts (solids components) of the carpet lining compound whose main components are co-polymer latex and inorganic fillers.

25 The co-polymer latex used in this invention may be styrene-butadiene latex, styrene-methylmethacrylate-butadiene latex, methylmethacrylate-butadiene latex, acrylonitrile-butadiene latex, natural latex,  
30 polyvinylchloride latex, ethylene-polyvinylchloride latex, ethylene-vinylacetate latex, acryl latex, etc. The co-polymer can also be prepared by co-polymerizing monomers with active groups such as carboxylic group, amide group, N-methylol group, glycidyl group, and  
35 hydroxyl group.

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The inorganic fillers used in this invention may be calcium carbonate, aluminum hydroxide, magnesium hydroxide, clay, barium sulphate, silica, silicates, titanium oxide, magnesium carbonate, etc., but not restricted to those listed. These inorganic fillers may be used as a single additive or as a combination of two or more components.

Incidentally, the mixing ratio for these inorganic fillers may be 30-750 weight parts, or more preferably 50-700 weight parts, against 100 weight parts of the aforementioned co-polymer latex. The use of the filler at less than 30 weight parts is not economical because of the large ratio of the co-polymer latex required. On the other hand, the use of more than 750 weight parts is also undesirable because of the loss in the carpet bonding strength and the thread pulling strength.

The graphite fibril which is the most significant part of this invention is added at 0.5-20 weight %, or preferably at 1-15 %, against 100 weight parts of the compound. A ratio less than 0.5 weight % does not give the intended static characteristics. On the other hand, a ratio greater than 20 weight % is not only uneconomical due to the high cost but also does not provide a drastic improvement in the static characteristics.

The graphite fibril used in this invention is a carbon fiber whose diameter is 3.5-70 nm, and its length is at least 5 times the diameter or more preferably 50-300 times the diameter of the fiber. The surface of said graphite fibril may be treated with ozone or nitric acid.

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The graphite fibril used in this invention can be produced by contacting suitable metal containing particles (for example, iron, cobalt, or nickel with alumina carrier) with a suitable carbon containing gaseous compound (for example, carbon monoxide) at 850-1200°C under a suitable pressure (for example 0.1-10 atmospheric pressure) for a desirable period of time (for example 10 seconds-180 minutes) as described in the specification sections of Japanese Patent Gazette Sho-62-500943, Japanese Patent Gazette Sho-63-503555, and US Patent 4,663,230, where the dry weight ratio of the carbon containing compound to the metal containing particles is at least 100:1 (gas phase method). The graphite fibril preferably used in this invention is an annular fibril which consists of concentrically arranged continuous outer layers made of systematically aligned carbon molecules similar to graphite, and an inner core layer which is either hollow or filled with carbon molecules with less systematic alignment compared to the outer layers. Further, it is desirable that the diameter of the aforementioned inner core layer be greater than 2 nm.

The graphite fibril specified above is explained in detail in the specification sections of Japanese Patent Gazette Sho-62-500943, Japanese Patent Gazette Sho-63-503555, and US Patent 4,663,230. The contents included in these Gazette Patents and the US Patent comprise the specification of this invention by virtue of reference.

When the diameter of the graphite fibril exceeds 70 nm, a decrease in static charge becomes insufficient due to the non-uniform dispersion and orientation of fibrils, and it also gives poor viscosity stability during the manufacturing process.

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Incidentally, it is desirable to disperse the graphite fibrils used in this invention in water by using an anionic surfactant before it is added to the co-polymer latex. Colophonium salts such as potassium colophionate or sodium colophionate, fatty acid salts such as potassium laurate, sodium laurate, potassium stearate, or sodium stearate, sulfuric ester salt of aliphatic alcohol such as laurylsodiumsulphonate, sodium or potassium salt of the condensate of dodecylbenzene sulphonate or naphthylsulphonate formaldehyde, sulphonates such as alkylnaphthylene sodiumsulphonate, etc. can be listed as anionic surfactant for this purpose. Among these materials, sulphonate type anionic surfactants are preferred. The use of a sodium or potassium salt of naphthylsulphonate formaldehyde condensates is particularly preferred. The addition of graphite fibrils directly into the latex in a powder form is not desirable because it reduces the stability of the latex, and creates solids precipitations. The use of surfactants other than anionic surfactants is also undesirable because of the solids precipitation and the poor stability caused by their relatively poor water dispersing nature.

The properties of the compound prepared according to this invention are normally adjusted by using water or viscosity increasing agents so that its viscosity is adjusted within 20,000-40,000 cps, or preferably within 25,000-35,000 cps, and its solids content becomes 60-83 weight % or preferably 63-80 weight %. In summary, when the viscosity of the aforementioned compound is below 20,000 cps, penetration of the compound into the carpet becomes too great and also the bonding strength becomes low. On the other hand, when the viscosity exceeds 40,000 cps,

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applicability becomes poor resulting in a non-uniform lining. Further, the solids content of the aforementioned compound at below 60 weight % is not desirable as the drying efficiency becomes poor due to the large amount of water, resulting in a poor thread pulling strength and bonding strength. The concentration above 83 weight % is also undesirable as it causes poor application efficiency and non-uniform application due to the high viscosity, resulting in a loss of qualities such as bonding strength and thickness uniformity.

As it is described above, the carpet lining compound manufactured by this invention is mainly composed of co-polymer latex and inorganic fillers, but it can also contain dispersants, antifoams, bridging agents, viscosity increasing agents, foaming agents, coloring agents, anti-combustion agents, antiseptic agents, pH adjusting agents, etc.

This invention is explained by using application examples. The expression of parts used in these application examples are on a weight basis unless specified otherwise.

Carpet lining compounds were prepared in Application Example 1, 2, and Reference Examples 1 through 7 using the mixing ratios listed below. Product properties were tested for each carpet prepared using these compounds, and the results were listed in Table 1.

Mixing Recipe		(Weight Parts)
30	Copolymer Latex	100 (solid components)
	Potassium Pyrrolinate	0.7
	Calcium Carbonate	400
	Anti-Aging Agent (Phenol Type)	1.0
	Anti-Static Agent	Shown in Table 1
	Viscosity Increasing Agent	1.0

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The carpet lining compounds were prepared by adding potassium pyrrolinate at first as a dispersant into the co-polymer latex, and then filler and anti-static agent were added and completely dispersed. The viscosity increasing agent and water were added in order to adjust the solids content to 70% and the viscosity to about 30,000 cps (measured by Brookfield viscometer BM Model No. 4 at 6 rpm).

#### Evaluation of Carpet Properties

Bonding strength and thread pulling strength of each carpet were measured.

The carpet lining compositions were coated onto the Toughtread Carpet whose primary base fabric was polypropylene fiber and the main fabric was nylon at 1300 g/sq.m (wet basis), and the 8-ounce jute secondary base fabric was pressed behind. The measurements were done after drying them at 120°C for a period of 20 minutes.

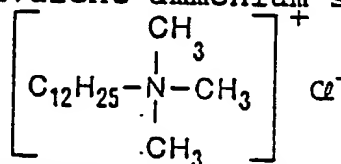
Subsequently, the static charge voltage was measured as an indication of the static characteristics according to the JIS Stroll Method (20°C, 20% RH).



Table 1

	Example 1	Example 2	Reference 1
Copolymer Latex (Solids)	Stylene- Butadiene Latex 100	PVC Latex 100	Stylene- Butadiene Latex 100
Inorganic Filler CaCO <sub>3</sub>	400	400	400
Anti-Static Agent			
(1) Alkylphosphate			
(2) Cationic Quadrivalent Ammonium Salt			
(3) Carbon Fibers			
(4) Graphite Fibril	12(2.3) *	12(2.3) *	
(5) Carbon Black			
Solid Components (%)	70	70	70
Viscosity of Composition (cp)	30,000	29,500	29,000
5-Day Viscosity (cp)	30,500	30,000	30,000
Carpet Properties			
Bonding Strength (Kg/5cm)	3.0	2.8	3.0
Thread Pulling Strength (Kg/pile)	3.1	3.0	3.0
Carpet Static Charge Voltage (KV)	0.04	0.04	3.0

\* Number in ( ) represents the weight % of anti-static agent in the solids component.



Lauriltrimethylammonium chloride

- (3) Carbon Fiber: Electric conductive carbon fiber (Toray Carbon Fiber, T300-3K, Diameter 6-7 microns, length 10 microns or longer)
- (4) Graphite Fibril: (diameter 30 nm, length 30 microns)
- (5) Carbon Black: Electric conductive carbon (Lion Kechen Black EC)

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Table 1 (Continued)

	Reference 2	Reference 3	Reference 4
Copolymer Latex (Solids)	Styrene- Butadiene Latex 100	PVC Latex 100	Styrene- Butadiene Latex 100
Inorganic Filler $\text{CaCO}_3$	400	400	400
Anti-Static Agent			
(1) Alkylphosphate	12(2.3) *		
(2) Cationic Quadrivalent Ammonium Salt		12(2.3) *	
(3) Carbon Fibers			12(2.3) *
(4) Graphite Fibril			
(5) Carbon Black			
Solid Components (%)	70	70	70
Viscosity of Composition (cp)	28,500	30,500	29,800
5-Day Viscosity (cp)	29,800	30,000	40,000
Carpet properties			
Bonding Strength (Kg/5cm)	2.2	2.4	2.4
Thread Pulling Strength (Kg/pile)	2.6	2.5	2.3
Carpet Static Charge Voltage (KV)	0.55	0.51	0.15

Table 1 (Continued)

	Reference 5	Reference 6	Reference 7
Copolymer Latex (Solids)	Stylene- Butadiene Latex 100	PVC Latex 100	Stylene- Butadiene Latex 100
Inorganic Filler CaCO <sub>3</sub>	400	400	400
Anti-Static Agent			
(1) Alkylphosphate			
(2) Cationic Quadrivalent Ammonium Salt			
(3) Carbon Fibers			
(4) Graphite Fibril	1(0.2)*	150(23)*	
(5) Carbon Black			12(2.3)*
Solid Components (%)	70	70	70
Viscosity of Composition (cp)	30,000	29,000	29,000
5-Day Viscosity (cp)	31,000	43,500	30,000
Carpet properties			
Bonding Strength (Kg/5cm)	3.0	2.6	3.0
Thread Pulling Strength (Kg/pile)	2.9	2.8	2.6
Carpet Static Charge Voltage (KV)	2.9	0.04	1.1

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Results

In Application Example 1 and 2, both carpet bonding strength and thread pulling strength were high and the static charge voltage was low, indicating the production of a carpet with satisfactory properties.

Reference Example 1 which was made without anti-static agent, clearly showed a high static charge voltage indicating unsatisfactory static prevention.

Reference Examples 2 and 3 used alkylphosphate and cationic quadrivalent ammonium salt as an anti-static agent respectively. These examples showed relatively low bonding strength and thread pulling strength. The static charge voltages were also higher compared to the figures for Application Example 1 and 2.

Reference Example 4 used conductive carbon fiber available in the market which had a larger diameter than the fiber diameter covered by this invention. Although this example gave a low static charge voltage, carpet bonding strength and thread pulling strength were both relatively low. It also showed a significant time-dependency of the viscosity of the compound.

In Reference Examples 5 and 6, mixing ratios of the graphite fibril were outside the range specified in this invention. Reference Example 5 showed a high static charge voltage, while Reference Example 6 showed a significant time-dependency of viscosity.

In summary, the carpet lining compounds covered by this invention are manufactured by adding graphite fibril in co-polymer latex, and they offer improved workability and viscosity stability during the production process, and they are effective as a binder for manufacturing static-free carpet.

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### B. Electroconductive Rubber Compounds

This invention offers electroconductive rubber compounds composed of rubber like-polymer (I), carbon fibrils (II) whose diameters are within 3.5-70 nm and their lengths are at least 5 times the diameter, and a (metha)acryloxy type silane coupling agent (III), where the weight ratio between the polymer (I) and the carbon fibrils (II) is 100: 1-50, and further the weight ratio between the carbon fibrils (II) and the coupling agent (III) is 100:1-50.

A single or a blend of two or more kinds of materials commonly used in the rubber industry may be used as the rubber-like polymer (I) in this invention. For example, natural rubber, polyisoprene rubber, polybutadiene rubber, butadiene-styrene co-polymer rubber, butadiene-acrylonitrile co-polymer rubber, polychloroprene rubber, ethylene.a-olefin type co-polymer rubber, ethylene.acryl co-polymer rubber, ethylene.vinylacetate co-polymer rubber, acrylic rubber, epichlorohydrin rubber, halogenated polyethylene, chlorosulfonated polyethylene, silicon rubber, fluoride rubber, and phosphagen rubber, etc. can be listed.

In addition, derivatives of the above listed rubbers such as derivatives obtained by adding maleic anhydride, a,b-unsaturated carboxylic acids and their esters, various vinyl compounds, and acetonaphthene derivatives, derivatives obtained by hydrogenation of the unsaturated groups in the main polymer chains can also be used.

Although, butadiene-acrylonitrile co-polymer rubber, ethylene.a-olefin co-polymer rubber, acrylic rubber, halogenated polyethylene, chlorosulfonated polyethylene, ethylene.vinylacetate co-polymer, silicon rubber, fluoride rubber, etc. are preferably used, butadiene-acrylonitrile co-polymer, ethylene.a-olefin co-polymer rubber, ethylene.vinylacetate co-polymer, silica on rubber, fluoride rubber are preferable.

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Dimensions of the carbon fibrils (II) used in this invention are 3.5-70 nm in diameter and at least 5 times the diameter in length, or preferably 3.5-40 nm in diameter and 100-10,000 times the diameter in length.

5 When the diameter exceeds 70 nm, its effect of imparting electroconductivity becomes poor, while a diameter less than 3.5 nm causes difficulty in handling as the fibers tend to scatter. When the length of the fiber is less than 5 times the diameter, the effects of  
10 imparting electroconductivity become small.

The carbon fibrils (II) can be manufactured by, for example, USP 4,663,230.

The carbon fibrils may be surface-treated with ozone, nitric acid, or monomers.

15 The carbon fibrils preferably used in this invention are essentially annular carbon fibrils consisting of concentrically arranged continuous outer layers made of systematically aligned carbon molecules, and an inner core layer. In addition, it is preferable  
20 that the inner core is hollow or filled with carbon molecules whose alignment is not as systematic as the carbon molecules in the outer layers, and the systematically aligned carbon molecules are in graphite form and further. The diameter of the inner core layer  
25 is preferably greater than 2 nm.

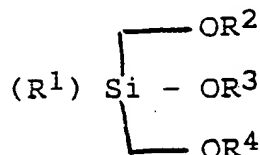
The graphite fibrils used in this invention can be produced by contacting suitable metal containing particles (for example, iron, cobalt, or nickel with alumina carrier) with a suitable carbon containing  
30 gaseous compound (for example, carbon monoxide) at 850-1200°C under a suitable pressure (for example 0.1-10 atmospheric pressure) for a desirable period of time (for example 10 seconds-180 minutes), where the dry weight ratio of the carbon containing compound to the  
35 metal containing particles is at least 100:1.

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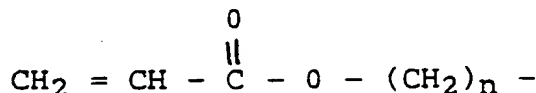
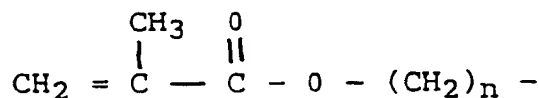
Desirable inter-crystalline distance of the carbon fibrils (II) measured by a Wide Angle X-Ray Refractometry is 3.38-3.50 angstroms, and its desirable refraction angle is 25.5-26.3 degrees.

The addition rate for the carbon fibrils (II) is 1-50 weight parts, or preferably 2-40 weight parts, against 100 weight parts of the rubber-like polymer (I). The amount of the carbon fibril (II) is selected within these ranges based on the required electroconductivity.

The silane coupling agents (III) used in this invention are acryloxy type materials which are preferably shown by the following formula.

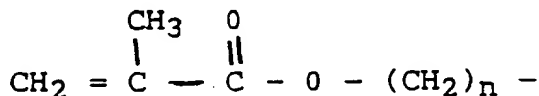


Where, R<sup>1</sup> is given by:



(n is an integer between 1-10)

Preferably



or still preferably the above formulae with n=3 are used.

Symbols R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> represent monovalent alkyl groups such as CH<sub>3</sub>-, C<sub>2</sub>H<sub>5</sub>-, C<sub>3</sub>H<sub>7</sub>-, C<sub>4</sub>H<sub>9</sub>-, etc. Preferably, CH<sub>3</sub>- and C<sub>2</sub>H<sub>5</sub>- groups can be listed.

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The silane coupling agents (III) used in this invention are considered to be effective in improving the dispersion characteristics of the carbon fibrils. The addition rate for the coupling agents is 1-50 weight parts, or preferably 1.5-25 weight parts, against 100 weight parts of the carbon fibrils (II).

When the addition rate for the silane coupling agent (III) is less than 1 weight part against 100 weight parts of the carbon fibrils (II), a stable electroconductivity cannot be obtained due to the poor dispersion of the carbon fibrils (II) into the rubber-like polymer (I). On the other hand, the addition of greater than 50 weight parts also adversely affects the electroconductivity of the resultant rubber compound.

The compounds produced by this invention may be mixed by using mixing devices such as rolls, kneader, Banbury Mixer, or extruder. Mixing by the Wet Master batch method is also possible.

Fillers such as other kinds of carbon fibrils, carbon black, silica, diatomaceous earth, crushed quartz, talc, clay, mica, calcium silicate, magnesium silicate, crushed glass, calcium carbonate, barium sulfate, zinc carbonate, titanium oxide, alumina, glass fibers, other types of carbon fibers, and organic fibers, known additives such as softener, plasticizer, handling aid, lubricant, anti-aging agent, and ultraviolet absorbing agent, etc. can also be added as desired.

The compounds manufactured by this invention may be molded by using the press vulcanization method, etc. after adding bridging agents using a commonly used method such as rolling.

This invention is explained in further detail by using application examples.



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The workability of the products produced in the Application Examples and Reference Examples was determined by checking the degree of the wrapping capability when these compounds were wrapped on 6-inch rolls at 50°C. The creation of a squeaking noise by the rolls was also checked at the same time.

The intrinsic volume resistivity which is an indication of electroconductivity was determined by coating the two ends of a sample strip whose dimensions were 2 cm wide by 6 cm long by 2 mm thick with 5 mm silver paste, and measuring the electrical resistance between these ends (SRIS: Measurement of Volume Resistivity of Electroconductive Rubber and Plastics by Japan Rubber Association Rubber Standard 2301-1969).

Other properties were determined based on JIS K6301.

#### Application Examples 1-3

Fluoride rubber (JSR Afras 150P, Japan Synthetic Rubber Co., Ltd.) as the rubber-like polymer (I), carbon fibers whose diameter was 10 nm, length 10 microns, inter-crystalline distance measured by the wide angle X-Ray Refractometry 3.45 angstroms, its refraction angle 25.8° as the carbon fibrils (II), and r-methacryloxytrimethoxy silane as the silane coupling agent (III) were used.

The rubber compounds were prepared by following the recipe shown in Table 1, and kneading them with 6-inch rolls.

The mixtures were subsequently press vulcanized at 170°C for a period of 20 minutes, and then oven vulcanized at 200°C for a period of 4 hours prior to measuring their properties and intrinsic volume resistivities.

The results are shown in Table 1.

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Reference Examples 1-6

As it is shown in Table 1, Reference Example 1 did not use silane coupling agent.

Reference Examples 2 and 3 are examples where the silane coupling agent used in Application Example 1 is replaced with r-glycidoxypropyltrimethoxy silane and N-(b-aminoethyl)r-aminopropyltrimethoxy silane respectively.

Reference Examples 4 and 5 are examples in which the carbon fibril (II) is replaced with other carbon fibers (A-6000: Asahi Carbon Fiber Company, (diameter 7 microns, length 6mm)) and electroconductive carbon particles (Ketchen Ec-DJ500: Lionakuzo Co., Ltd.) respectively.

Reference Example 6 is an example in which the addition rate of the carbon fibril (II) is changed to 1 weight part.

The procedures used for Reference Examples 1-6 are the same as those used for Application Example 1 except that the above described changes were made.

The results are shown in Table 1.

Application Examples 4, 5

Ethylene.a-olefin type co-polymer rubber (EP21L: Japan Synthetic Rubber Co., Ltd.) as the rubber-like polymer (I), carbon fibril (II) whose diameter was nm and length was 10 mm, and r-methacryloxytrimethoxy silane as the silane coupling agent (III) were used.

The mixtures prepared by following the recipe shown in Table 1 were kneaded for a period of 5 minutes using a Plast Mill.

The rubber compounds removed from the Plast Mill were tested for workability using 6-inch rolls.

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Subsequently, vulcanizing agents shown in Table 1 were added, and vulcanized at 150°C for a period of 20 minutes by the press vulcanization method. Properties and intrinsic volume resistivity were measured at the end.

The results are shown in Table 1.

Reference Examples 7, 8

Reference Example 7 represents an example in which the addition rate of the carbon fibril was changed to 60 weight parts.

Reference example 8 represents an example in which the carbon fibril (II) was replaced with carbon black (HAF, 30 micron carbon particles).

The procedures used for Reference Examples 7, 8 were the same as those used for Application Example 4 except that the above described changes were made.

The results are shown in Table 1.

Application Examples 6, 7

Silicon rubber (JSR EH524OU, Japan Synthetic Rubber Co., Ltd.) as the rubber-like polymer (I), carbon fibril (II) whose diameter was 10 nm and length was 10 mm, and r-methacryloxytrimethoxy silane as the silane coupling agent (III) were used. Various additives were added using 6-inch rolls.

The mixtures were subsequently press vulcanized at 170°C for a period of 10 minutes, and then oven vulcanized at 200°C for a period of 4 hours prior to measuring their properties and intrinsic volume resistivities.

The results are shown in Table 1.

Reference Example 9

Using the same procedures as the procedures used for Application Example 6 except that the carbon fibril (II) was replaced with electroconductive carbon (Ketchen EC-DJ500).

The results are shown in Table 1.

Table 1

	Application Example						
	1	2	3	4	5	6	7
[Recipe] (weight parts)							
Rubber-like polymer (I)							
EP21				100	100		
AFRAS 150P	100	100	100				
EH5240U						100	100
Carbon Fibril (II)	5	10	25	20	40	5	10
Methacryloxy Silane							
Coupling Agent (III)							
r-methacryloxy propyl trimethoxy silane	1	1	1	1	1	1	1
Other Additives							
Stearic Acid				1	1		
Sodium Stearate	2	2	2				
Zinc White #1				5	5		
HAF Carbon (N-330)							
Ketchen EC DJ500							
Carbon Resin (A-6000)							
r-glysidoxypentyl trimethoxy silane							
N-(b-aminoethyl)-r-amino propyltrimethoxy silane							
Nocceller CZ*1				1.5	1.5		
Sunseller-TRA*1				0.75	0.75		
Sunseller-TL*1				0.75	0.75		
Triallylisocyanate*2	5	5	5				
Parkadox14*3	1	1	1				
Sulfur*3				1.5	1.5		
JC-8*3						0.5	0.5
[Evaluation Results]							
Workability	0	0	0	0	△	0	0
100% Tensile Stress (Kgf/sp.cm)	90	146	-	68	135	21	33
Tensile Strength (Kgf/sq.cm)	205	236	358	141	224	75	83
Elongation (%)	260	230	100	330	240	300	270
Hardness (JIS A)	78	87	97	82	93	65	77
Intrinsic Volume (Ohm-cm)	76	12	0.2	9	0.9	5100	21
Resistivity Min/Max	/101	/21	/0.7	/16	/1.8	/5600	/32

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Table 1 (Continued)

	Reference Example				
	1	2	3	4	5
[Recipe] (weight parts)					
Rubber-like polymer (I)					
EP21					
AFRAS 150P	100	100	100	100	100
EH5240U					
Carbon Fibril (II)	5	5	5		
Methacryloxy Silane					
Coupling Agent (III)					
r-methacryloxy propyl trimethoxy silane				1	1
Other Additives					
Stearic Acid					
Sodium Stearate	2	2	2		
Zinc White #1					
HAF Carbon (N-330)					
Ketchen EC DJ500				10	
Carbon Resin (A-6000)					25
r-glycidoxypentyl trimethoxy silane		1			
N-(b-aminoethyl)-r-amino propyltrimethoxy silane			1		
Nocceller CZ*1					
Sunseller-TRA*1					
Sunseller-TL*1					
Triallylisocyanate*2	5	5	5	5	5
Parkadox14*3	1	1	1	1	1
Sulfur*3					
JC-8*3					
[Evaluation Results]					
Workability	0	0	0	Δ	Δ
100% Tensile Stress (Kgf/sp.cm)	72	65	79	74	-
Tensile Strength (Kgf/sq.cm)	195	147	184	219	217
Elongation (%)	270	210	240	280	50
Hardness (JIS A)	77	75	77	82	77
Intrinsic Volume (Ohm-cm)	210	6	6	2530	55
Resistivity Min/Max	/1015	>10	>10	/3970	/87

Table 1 (Continued)

	Reference Example			
	6	7	8	9
[Recipe] (weight parts)				
Rubber-like polymer (I)				
EP21		100	100	
AFRAS 150P	100			
EH5240U				100
Carbon Fibril (II)	1	60		
Methacryloxy Silane				
Coupling Agent (III)				
r-methacryloxy propyl trimethoxy silane	1	1		1
Other Additives				
Stearic Acid			1	
Sodium Stearate				
Zinc White #1			5	
HAF Carbon (N-330)			40	
Ketchen EC DJ500				10
Carbon Resin (A-6000)				
r-glycidoxypropyl trimethoxy silane				
N-(b-aminoethyl)-r-amino propyltrimethoxy silane				
Nocceller CZ*1		1.5	1.5	
Sunseller-TRA*1		0.75	0.75	
Sunseller-TL*1		0.75	0.75	
Triallylisocyanate*2	5			
Parkadox14*3	1			
Sulfur*3		1.5	1.5	
JC-8*3				0.5
[Evaluation Results]				
Workability	0	X	△	△
100% Tensile Stress (Kgf/sp.cm)	42		42	22
Tensile Strength (Kgf/sq.cm)	153		193	71
Elongation (%)	430		420	350
Hardness (JIS A)	57		75	65
Intrinsic Volume (Ohm-cm)				103
Resistivity Min/Max	>10 <sup>6</sup>		>10 <sup>6</sup>	/218

\*1: Vulcanization Accelerator

Nocceller-CZ:

N-Cyclohexyl-2-benzothiazyl-sulfonamide

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TABLE 1 FOOTNOTES

\*1: Vulcanization Accelerator

Nocceller-CZ: N-Cyclohexyl-2-benzothiazyl-sulfonamide

Sunseller-TRA: Dipentamethylenethiuram tetrasulfide

Sunseller-TL: Tellurium diethyldithiocarbamate

5 \*2: CO-Agent

\*3: Vulcanization Agent

Parkadox 14: 1,3 Bis-(t-butylperoxy-iso-propyl)-benzene

JC-8: 2,5-Di-methyl-2,5-di(t-butylperoxy)-hexane/silicon  
rubber=1/1 paste

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The rubber compounds produced by this invention have superior electroconductivity compared to the compounds with the same amount of carbon black addition, and also have very small variation in electroconductivity. Further, the amount of carbon fiber required for obtaining the same level of electroconductivity is smaller than the amount of carbon black required, and handling and workability are also superior.

The compounds covered by this invention can be utilized for manufacturing static-free rolls, belts, hoses, floor materials, power wires, electrodes, semi-conductive layers of and cables, and grounding wire.

#### C. Rubber Compounds

As a result of strenuous efforts for solving the aforementioned problems discussed in under the Background of the Invention, the inventors of this invention discovered that the addition of a small amount of special carbon fibril to rubber significantly increased its hardness. Further investigation proved a surprising fact, that the addition of 1/2 the amount of the commonly used carbon black (for example, HAF grade) gave an increase in the hardness as compared to the carbon black.

As a result of further research on the industrial applications of this discovery, the inventors discovered that the addition of a suitable amount of the special carbon fibril covered by this invention to a single or a combination of rubbers available in the market results in a vulcanized rubber with a high hardness, superior workability, and a high breaking strength, improved abrasion resistance, improved thermal deterioration resistance, and low heat generation.



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In summary, this invention relates to a rubber compound consisting of 100 weight parts of natural and/or synthetic rubber and 5-90 weight parts of carbon fibrils, where these carbon fibrils are agglomerations of fibers whose diameters are within 3.5-70 nm, whose lengths are greater than about 100 times the diameters, the maximum diameter of the agglomeration of fibers is less than 0.25 mm, and the content of the fibrils whose agglomerated diameters fall within 0.10-0.25 mm is greater than 50%.

In a separate effort for developing a new material for the TBR tread, the inventors also discovered that the addition of a small amount of the aforementioned carbon fibril to rubber significantly increased hardness and elongation stress at a low elongation range. It was further discovered that the replacement of part of the commonly used high-reinforcement carbon black with the said carbon fibril could surprisingly maintain the hardness and the elongation stress at a low elongation range at the same level even when the amount of the fibril is 1/2-1/4 of the carbon black.

Therefore, the inventors pursued the research on the industrial application of this discovery. As a result, they confirmed that a vulcanized rubber with superior breaking strength, tear strength, abrasion resistance, and with low density and low heat generation could be produced while maintaining the hardness and the low elongation stress of the rubber obtained without the replacement, by replacing a part of the carbon black added to the rubber, which was mainly composed of natural rubber, with a small amount of the special carbon fibril covered by this invention.

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In summary, this invention relates to a rubber compound consisting of 100 weight parts of rubber, which contains at least 50% of natural rubber, 5-60 weight parts of carbon black, and 1-30 weight parts of carbon fibrils, where these carbon fibrils are agglomerations of fibers whose diameters are within 3.5-70 nm, whose lengths are greater than about 100 times the diameters, the maximum diameter of the agglomeration of fibers is less than 0.25 mm, and the content of the fibrils whose agglomerated diameters fall within 0.10-0.25 mm is greater than 50%.

As a result of the additional research work for developing a new material for oil-seal, they discovered that the rubber compound characterized by the addition of 1-30 weight parts, or preferably 5-20 weight parts, of the aforementioned special carbon fibril to 100 weight parts of an oil resistant rubber had relatively small surface friction resistance while its mechanical strengths were maintained.

The aforementioned oil resistant rubber is a rubber which causes relatively small swelling when it is contacted with lubricant oils. For example it may be fluoride rubber, acryl rubber, hydrin rubber, silicon rubber, acrylonitrile-butadiene co-polymer rubber (NBR), ethylene-acrylester rubber, chlorosulphonated polyethylene, chloroprene rubber, etc. However, fluoride rubber, acryl rubber, and NBR are preferred.

The carbon fibril used in this invention can be produced by contacting suitable metal containing particles (for example, iron, cobalt, or nickel with alumina carried) with a suitable carbon containing gaseous compound (for example, carbon monoxide at 850-1200°C under a suitable pressure (for example, 0.1-10 atmospheric pressure) for a desirable period of

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time (for example, 10 seconds - 180 minutes) as described in the specification sections of Japanese Patent Gazette Sho-62-500943, and US Patent 4,663,230, where the dry weight ratio between the carbon containing compound and the metal containing particles is at least 100:1 (gas phase method).

The diameter of the carbon fibril produced by the aforementioned method is within 3.5-70 nm, or preferably within 3.5-40 nm, and its length is greater than about 100 times the diameter. The carbon fibril preferred in this invention is an annular fibril which consists of concentrically arranged outer layers whose carbon molecules are systematically aligned, and an inner core layer which is either hollow or filled with carbon molecules with less systematic alignment as compared to the outer layers. It is further desirable that the carbon in the aforementioned outer layers is of graphite form, and the diameter of the aforementioned inner core layer is greater than 2 nm.

The desirable crystalline distance of the aforementioned carbon fibril measured by Wide Angle X-Ray Refractometry is within 3.38-3.50 angstroms, and the desirable refraction angle is within 25.5-26.3 degrees.

The carbon fibril specified above is explained in detail in the specification sections of Japanese Patent Gazette Sho-62-500943 and US Patent 4,633,230. The contents included in the Patent Gazette and the US Patent compose the specification of this invention by virtue of reference.

The carbon fibrils used in this invention must have the form of intertwined agglomerations whose diameters are within the specified range. It is essential that the carbon fibrils used in this invention

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are in the form of inter-twined agglomerations in order to increase the hardness while maintaining the breaking strength of the vulcanized rubber on the one hand, and in order to prevent the deterioration in the hardness and the low elongation stress with the addition of carbon fibrils less than the amount of carbon black replaced on the other hand. The carbon fibrils should be as narrow as possible in their diameter, and as long as possible in their length in order to prevent untangling. The dimensional specifications for the carbon fibrils used in this invention satisfy these conditions. In addition, carbon fibrils whose surfaces are treated with ozone, nitric acid, or monomers can also be suitably used.

The dimensions of the agglomerations contained in the carbon fibrils produced by the aforementioned method are not uniform, and a significant amount of agglomerations whose diameters are greater than 0.25 mm is normally contained. Carbon fibrils whose maximum agglomeration diameter is smaller than 0.25 mm, and the content of the agglomerations whose diameter fall within 0.10-0.25 mm is greater than 50%, can be obtained by treating an untreated carbon fibril in a vibration type ball mill. For example, 500 g of steel balls whose diameter is 12.8 mm, and 50 g of untreated carbon fibril are fed in a 800 cc stainless steel vessel, and milled at 1720 rpm for a period of 35 minutes. This treatment method is only an example, and therefore it is not intended to restrict the treatment method.

When agglomerations whose diameters are greater than 0.25 mm are contained in the carbon fibril, dispersion of the carbon fibril into the rubber compound becomes poor during the kneading process, which in turn lowers the breaking strength of the vulcanized rubber.

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Likewise, if the content of the agglomerated carbon fibril whose diameters fall within 0.10-0.25 mm is below 50%, not only sufficient hardness cannot be obtained but also maintaining of the low elongation stress level and breaking strength of the vulcanized rubber becomes difficult.

In the manufacturing of high-hardness rubber compounds, 5-90 weight parts of the carbon fibril is mixed with 100 weight parts of the rubber component. When the mixing ratio is below 5 weight %, the intended increases in hardness, breaking strength, and abrasion resistance of the vulcanized rubber cannot be obtained. On the other hand, if the mixing ratio exceeds 90 weight %, mixing of the carbon fibril into the rubber becomes difficult resulting in a poor dispersion which in turn results in a drastically reduced breaking strength of the vulcanized rubber.

In the manufacturing of a new TBR tread material, 1-30 weight parts or preferably 5-25 weight % of the carbon fibril is mixed with 100 weight parts of the rubber component. When the mixing ratio is below 1 weight %, significant effects of the addition cannot be achieved. On the other hand, if the mixing ratio exceeds 30 weight %, both hardness and low elongation stress value become too high, and breaking strength becomes lower as a result of the low tensile breaking length.

Although there is no particular restriction on the type of carbon black used, it is preferable to use a high-reinforcing type carbon black whose particle size is less than 40 millimicrons, iodine absorption is above 60 mg/g, and DBP absorption is above 0.95 cc/g. It is also possible to use other types of carbon black and/or other carbon fibrils as a combination as required.

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The mixing ratio for the carbon black is 5-60 weight parts, or more preferably 10-45 weight parts, against 100 weight parts of the rubber component. When the mixing ratio is below 5 weight parts, significant effects of the addition cannot be achieved and it becomes difficult to maintain the desired levels of hardness and low elongation stress. On the other hand, if the mixing ratio exceeds 60 weight parts, both high elongation stress and breaking strength become lower due to the drastic loss of elongation-crystallization phenomenon of the natural rubber.

Although there is no particular restriction on the type of rubber component used in the case of manufacturing a high-hardness rubber, natural rubber is most suitable as the base rubber component for the manufacturing of a new type of TBR tread material. When a blend of natural rubber and a synthetic rubber is used as the base rubber, high elongation stress and breaking strength of the vulcanized rubber are reduced as the content of the synthetic rubber increases due to the loss of the elongation-crystallization phenomenon.

The mixing ratio for the carbon fibril in the case of oil-seal compound is 1-30 weight parts, or more preferably 5-20 weight parts, against 100 weight parts of the rubber component. When the mixing ratio is below 1 weight part, effects of the improving friction resistance is insufficient, while the addition of more than 30 weight parts tends to increase the viscosity and therefore results in a poor workability.

As synthetic rubbers used in this invention, emulsion polymerized styrene-butadiene rubber, solution polymerized styrene-butadiene rubber, polybutadiene rubber, polyisoprene rubber, ethylene-propylene rubber, acrylonitrile-butadiene rubber, butyl rubber,

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polychloroprene rubber, acryl rubber, fluoride rubber, chlorinated polyethylene rubber, chlorosulphonated polyethylene, epichlorohydrin rubber, silicone rubber, etc. can be listed. These synthetic rubbers are also used together with natural rubber in the manufacturing of TBR tread materials whose main component is natural rubber.

In the compounds covered by this invention, additives commonly used in the rubber industry such as vulcanizing agents, vulcanizing accelerators, vulcanizing acceleration aids, anti-aging agents, softeners, and fillers can be added as required. Compounding of these additives is done by kneading them with the rubber components at first using a commonly used kneading device such as rolls or Banbury Mixer, and then molding and vulcanizing under normal conditions for vulcanized rubber manufacturing.

Incidentally, mixing of the carbon fibrils and the rubber component used in this invention can also be achieved by the Wet Master Batch method.

This invention will be explained in detail by using application examples. However, this invention is not restricted by these applications examples.

Incidentally, measurement of the diameter of the carbon fibril is done by the following procedures.

After gold plating the surface of the double-sided adhesive tape on which the sample is adhered, 12 spots of the surface were observed by using Hitachi S-510 SEM at x50 magnification. Three spots with average appearance were selected, and the maximum diameter and the area occupied by each agglomeration were measured. The content of the agglomerations whose diameters fall within 0.10-0.25 mm was obtained by the following equation, and it is reported as the average for the three measurements.

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Area occupied by agglomerations  
whose diameter is within 0.10-0.25

Content= \_\_\_\_\_ x 100

Area occupied by agglomerations

5     Application Examples I, II and Reference Examples I, II

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Mixing Recipe was as follows:

Mixing Recipe	(PHR)
JSR #1502	100
Carbon Fibril	40
10     Zinc White 1)	3
Stearic Acid 2)	2
Vulcanization Accelerator	0.6
Nocceler-D 3)	
Nocceler-DM 4)	1.2
15     Sulfur 5)	1.5
1) Sakai Chemical Industries No. 1 JIS K1410	
2) Kaoh Soap, JIS K3341	
3) Ohuchi Shiko, Diphenyl guanizine	
4)       , Dibenzothiazilsulfide	
20     5) Karuizawa Seiren, sulfur powder	

25     A 2 mm thick rubber sheet was prepared by kneading the above described mixture using a Laboplast mill and rolls, and subsequently vulcanizing it at 145°C for a period of 30 minutes. Samples were tested by the Tensile Testing method specified for vulcanized rubber in JIS K6301 standard in order to obtain the data on hardness (Hs) and breaking strength (TB) shown in Table 1.

30     As can be seen in Application Example I, the addition of the carbon fibrils covered by this invention at mixing ratio as small as 40 weight parts resulted in hardness as high as (Hs)=80, and breaking strength as high as 290 Kgf/sq.cm which is considered to be the highest level attained by the SBR #1502. On the other



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hand, as can be seen in Reference Example I, when carbon fibrils which contain agglomeration diameters greater than 0.25 mm are added, Hs can be easily increased but TB is significantly decreased.

- 5 By comparing Application Example II and Reference Example II, it is found that Hs is maintained at the normal level while TB is decreased if a large amount of agglomerations whose diameter is less than 0.10 mm is added.

Table 1

	Application Example I			Reference Example I		
Diameter of Agglomeration (mm)	>0.25	0.25 -0.10	<0.1	>0.25	0.25 -0.10	<0.10
Content (%) of Agglomeration	0	60	40	5	55	40
Carbon Fibril Mixing Ratio (PHR)		40			40	
Hs (JIS-A)		80			91	
TB (Kgf/sq.cm)		290			150	

Table 1 (Continued)

Application Example II			Reference Example II			Carbon Fibril Diameter=30nm Length=30 microns Crystalline distance by SEM refractometry 3.45 angstroms 25.8 degree
>0.25	0.25 -0.10	<0.10	>0.25	0.25 -0.10	<0.10	
0	70	30	0	20	80	
	40			40		
90				70		JIS K6301
310				230		JIS K6301

Application Example II and Reference Examples III through V

Table 2 shows examples of the effects of this invention based on additional evaluation items. The mixing ratios are as shown in Table 2, and the kneading and molding-vulcanizing methods are same as the method shown in Table 1.

Testing methods are based on JIS standards and ASTM standards as shown in Table 2. Testing for the rolling characteristics which is not specified in any of these standards is done by observing the behaviors of the unvulcanized rubber compound wrapped in a 10 inch rolling machine.

By comparing Application Example III and Reference Example V, it is found that Hs of the vulcanized rubber (Reference Example V) manufactured by adding 90 weight parts of normal carbon black (N330) and Hs of the compound manufactured by adding 45 weight parts of carbon fibril (Application Example III) are both as high as 90. This fact indicates that the carbon fibril covered by this invention can produce a high-hardness vulcanized rubber by adding only half the mixing ratio of carbon black. In addition, comparison of properties for these products indicates that TB and abrasion resistance for the Application Example were higher than for the Reference Example. Since the mixing ratio for the carbon fibril is only one half of the carbon black, the resultant vulcanized rubber has a high elasticity, which can also be judged by the low 25°C tan d value. This fact also suggests the low heat generation. When high hardness is required as mentioned earlier, it is obvious that the thermal deterioration characteristic becomes superior as compared to the vulcanized rubber with conventional sulfur mixing ratio since sulfur content can be maintained at the normal level when carbon fibril is used.

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Reference Example III represents an example with low carbon fibril content, in which Hs, TB, and abrasion resistance are drastically reduced.

5 Reference Example IV represents an example with a high carbon fibril content. Although a higher hardness can be obtained, workability is poor and TB and abrasion resistance are lower, while a greater 25°C tan d or a higher heat generation is expected.

Table 2

	Application Example II			Reference Example III			Reference	
Diameter of Agglomeration (mm)	>0.25	0.25	<0.10	>0.25	0.25	<0.10	>0.25	0.25
Content (%) of Agglomeration	0	~0.10 75	25	0	~0.10 75	25	0	~0.10 75
JSR SBR #1502		100			100			100
Carbon Fibril		45			3			100
Carbon Black		-			-			-
Asahi #70								
Naphthene oil		-			-			15
Zinc White		3			3			3
Stearic Acid		2			2			2
Vulcanization Accelerator								
Nocceler D		0.6			0.6			0.6
Nocceller DM		1.2			1.2			1.2
Sulfur		1.5			1.5			1.5
Rollability		OK			OK			X
Hardness (JIS-A)		90			56			98
Tensile Strength (Kgf/sq.cm)		340			102			110
Pico Friction (-)		100			80			48
Tensile Strength variation (%)		-28			-30			-42
25° Tan d		0.108			0.085			0.176

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Application Examples IV, V and Reference Examples VI, VII

Table 3 shows the comparison between the effectiveness of the normal carbon black (N-330- or N-990) and the carbon fibril covered by this invention on EPDM (Japan Synthetic Rubber Co., Ltd, JSR EP21) and Fluoride rubber (Japan Synthetic Rubber Co., Ltd, JSR Afras 150P).

Application Examples IV and V both gave a higher hardness and a higher tensile strength compared to Reference Examples VI and VII.

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Table 3

	Application Reference IV			Ref. Example VI	Reference Example V			Ref. Example VII
Diameter of Agglomeration (mm)	>0.25	0.25	<0.10	-	>0.25	0.25	<0.10	-
Content (%) of Agglomeration Diameter=30nm Length=30 microns	0	75	25	-	0	75	25	-
[Recipe] [wt. parts]								
EP21 (JSR Co., Ltd)	100			100				
Afras 150P (")					100			100
Stearic Acid	1			1				
Sodium Stearate					2			2
Zinc White #1	5			5				
HAF Carbon (N-330)				40				
MT Carbon (N-990)								25
Carbon Fibril	40				15			
Nocceler-CZ *1	1.5			1.5				
Sunseler-TRA *1	0.75			0.75				
Sunseler-TL *1	0.75			0.75				
Triallylisocyanate*2					5			5
Parkadox 14 *3					1			1
Sulfur *3	1.5			1.5				
[Evaluation Results]								
Rollability	OK			OK	OK			OK
Hardness (JIS-A)	93			75	91			72
100% tensile Stress (Kgf/sq.cm)	135			42	189			53
Tensile Strength (Kgf/sq.cm)	224			206	293			188
Elongation (%)	240			410	200			250

\*1: Vulcanization Accelerator

Nocceler-CZ: N-Cyclohexyl-2-benzothiazyl-sulfenamide

Sunseler-TRA: Dipentamethylenethiuram tetrasulfide

Sunseler-TL: Tellurium diethyldithiocarbamate

\*2: Co-Agent

\*3: Vulcanizing Agent

Parkadox 14: 1.3 Bis-(t-butylperoxy-iso-propyl)benzene

Application Examples VI through VII and Reference Examples VIII through XI

Table 4 and Table 5 represent examples confirming the effects of this invention in the manufacturing of new types of TBR tread and sidewall materials. The mixing recipes were as shown in Tables 4 and 5, and kneading procedures were as shown in Table 2. Aromatic oil Fukkol AROMAX #3 manufactured by Fuji Kosan and carbon black #80 manufactured by Asahi Kasei were used. The testing procedures were the same as those mentioned in Table 2. The DIN-Abrasion was measured following the DIN-53516 standard. Other additives were exactly same as listed in Table 2.

By comparing Application Example VI and Reference Example VIII, it is found that Application Example VI, in which 5 weight parts of carbon fibril covered by this invention was added in place of 20 weight parts reduction in the carbon black (N-220), had a comparable hardness while breaking strength (TB, TR), abrasion resistance were improved and heat generation was smaller (smaller tan d) compared to the Reference Example in which 50 weight parts of commonly used carbon black was used.

Reference Example X is the case where a high carbon fibril content is used, which obviously gave a large increase in hardness but gave a lower TB value.

Application Example VII and Reference Example XI shown in Table 5 shown the effects of carbon fibril when polybutadiene rubber (BR) is blended to natural rubber (NR) at NR/BR=70/30. Application Example VIII has improved breaking characteristics, abrasion resistance, and heat generation characteristics and has a lower density compared to Reference Example XI.

Table 4

	Appl. Example VI	Ref. Example VIII	Ref. Example IX	Ref. Example X
NR	100	100	100	100
Carbon Fibril	5	0	0.5	35
Carbon Black N-220	30	50	48	0
Aromatic Oil	5	5	5	5
Zinc White	5	5	5	5
Stearic Acid	2	2	2	2
Vulcanization Accl. CZ1*	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5
Hardness (JIS-A)	67	67	67	85
TB (Kgf/sq.cm)	354	330	332	236
TR (Kgf/sq.cm)	86	80	81	90
DIN Abrasion (-)*2	100	89	91	108
tan d 50°C *3	0.098	0.114	0.112	0.139
Density	1.084	1.122	1.110	1.112

\*1: N-Cyclohexyl-2-benzothiazyl-sulfenamide (Ouchi Shiko, Nocceler CZ)

\*2: DIN Abrasion Tester manufactured by Toyo Seki, Measurement for Application Example VI is assumed as 100.

\*3: Measured at 15Hz using RDS7700 manufactured by Leometrix Far East, Co. Ltd.

Table 5

	Application Example VII	Reference Example XI
NR	70	70
BR01	30	30
Carbon Fibril	5	0
Carbon Black N220	30	50
Carbon Black N774	-	-
Aromatic Oil	5	5
Zinc White	5	5
Stearic Acid	2	2
Vulcanization Accelerator CZ	1.0	1.0
Sulfur	1.5	1.5
Hardness (JIS-A)	65	65
TB (Kgf/sq.cm)	315	290
TR (Kgf/sq.cm)	83	75
DIN Abrasion (-)*2	100	87
tan d 50°C *3	0.103	0.130
Density	1.080	1.117

\* Reference Example XI is shown as the ratio when  
Application Example VII is assumed to 100.

Application Examples VIII through XI and Reference  
Examples XIII through XV



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Application Examples VIII through XI and Reference Examples XII through XV

Application Examples VIII through XI were prepared by kneading the additives shown in Table 6 with JSR Afras 150P (tetrafluoroethylene-propylene co-polymer: manufactured by Japan Synthetic Rubber) using a 6 inch roll.

Dimensions of the Carbon Fibril A used for Application Examples VIII through XI measured by an electron microscope were 300 nm in diameter and 30 microns in length, and the diameter and its content in fibril agglomeration were as follows:

Diameter of agglomerations:	0.11-0.25 mm	75 wt%
"	0.11-0.10 mm	25 wt%

Vulcanization was done in an oven at 200°C x 4 hours, following the press vulcanization at 170°C x 10 minutes.

Table 5 shows the results of property analyses.

Reference Example XII was kneaded and molded in the same procedures as Application Example 2 except that type (B) carbon fibril which contained 10 weight % fibril agglomeration whose diameter was within 0.26-0.50 mm was used. It showed inferior tensile strength and elongation compared with the Application Example.

In Reference Examples XIII through XV, carbon fibril was replaced with solid lubricants such as graphite (Reference Example VIII), Molybdenum sulfide (Reference Example XIV), polytetrafluorethylene (Reference Example XV), and compounds were prepared by following the mixing ratios shown in Table 7. Kneading, molding, and vulcanization procedures were the same as the procedures used in Application Examples VIII through XI. The results are shown in Table 7.

Reference Examples XIII through XV all showed inferior tensile strength and elongation compared to Application Examples.

Table 6

Application Example	VIII	IX	X	XI
[Recipe] (weight %)				
JSR Afras 150P	100	100	100	100
Carbon Fibril-A	5	10	20	5
MT Carbon				10
Sodium Stearate	1	1	1	1
Triallylisocyanate	5	5	5	5
Parkadox 14	1	1	1	1
(manufactured by Nooly Chem.)				
Total	112	117	127	122
[Characteristics]				
Properties				
Tensile Strength	185	225	295	183
(Kgf/sq.cm)				
Elongation (%)	250	210	180	260
Hardness	80	88	93	78
Oil Resistance (JIS #3 oil, 175°C x 70 hours)				
Swelling (%)	+18.2	+19.2	+19.6	+17.9
Hardness Change	-11	-10	-5	-12
Noony Viscosity	82	95	112	93
ML <sub>1+4</sub> (100°C)				

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Table 7

Reference Example	XII	XIII	XIV	XV
[Recipe] (weight %)				
JSR Afras 150P	100	100	100	100
Carbon Fibril-B	10			
Graphite		50		
Molybdenum sulfide			50	
Polytetrafluoroethylene				50
Sodium Stearate	1	1	1	1
Triallylisothianate	5	5	5	5
Parkadox 14	1	1	1	1
(manufactured by Nooly Chem.)				
Total	117	157	157	157
[Characteristics]				
Properties				
Tensile Strength (Kgf/sq.cm)	163	235	135	278
Elongation (%)	160	50	110	80
Hardness	87	89	83	96
Oil Resistance (Jis #3 oil, 175°C x 70 hours)				
Swelling (%)	+19.8	+17.3	+17.1	+15.4
Hardness Change	-11	-8	-7	-5
Noony Viscosity ML <sub>1+4</sub> (100°C)	101	167	115	136

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As it is discussed above, rubber compounds manufactured by this invention can provide vulcanized rubber with high hardness, superior breaking strength, abrasion resistance, and thermal deterioration characteristics, as well as low heat generation.

By effectively utilizing these characteristics, rubber parts and rubber products with superior properties which could not be obtained in the past can be easily manufactured. As the examples for such application, tread for large vehicles and automobile tires, sidewall and bead filler, power cable, hose, weather strips, gasket, sealing materials, high-hardness rubber rolls, glass run for automobiles, rubber sole of shoes, various high-hardness belts, high-hardness anti-vibration rubber, etc. can be mentioned. However, this invention is not restricted by these examples.

Further, by replacing a part of carbon black used for rubber compounds whose main component is natural rubber with the special carbon fibril covered by this invention, rubber compounds for TBR tread that can withstand severe conditions associated with high-load and high-speed can be obtained. Replacement of carbon black with only 1/2-1/4 the amount of carbon fibril can maintain the hardness and low elongation stress of the compound while drastically improving the characteristics such as breaking strength, tear strength, and abrasion resistance.

Other emodiments are within the following claims.

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Scope of the Patent Claims

1. Compounds for carpet lining materials characterized by the use of 0.5-20 weight % of graphite fibril, whose diameter is about 3.5-70 nm and its length is at least 5 times the diameter, against 100 weight parts (solid components) of the carpet lining material whose main components are co-polymer latex and inorganic fillers.
2. Electroconductive rubber compounds composed of rubber-like polymer (I), carbon fibrils (II) whose diameters are within 3.5-70 nm and their lengths are at least 5 times the diameter, and a (metha)acryloxy type silane coupling agent (III), where the weight ratio between the polymer (I) and the carbon fibrils (II) is 100: 1-50, and further the weight ratio between the carbon fibrils (II) and the coupling agent (III) is 100: 1-50.
3. Electroconductive rubber compounds covered by the descriptions in claim 2, where the carbon fibrils (II) are essentially annular carbon fibrils consisting of concentrically arranged continuous outer layers made of systematically aligned carbon molecules, and an inner core layer.
4. Rubber compounds consisting of 100 weight parts of natural and/or synthetic rubber and 5-90 weight parts of carbon fibrils, where these carbon fibrils are agglomerations of fibers whose diameters are within 3.5-70 nm, whose lengths are greater than about 100 times the diameters, the maximum diameter of the agglomeration of fibers is less than 0.25 mm, and the content of the fibrils whose agglomerated diameters fall within 0.10-0.25 mm is greater than 50%.

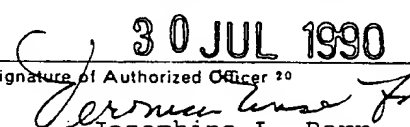
- 50 -

5. Rubber compounds consisting of 100 weight parts of rubber, which contains at least 50% of natural rubber, 5-60 weight parts of carbon black, and 1-30 weight parts of carbon fibrils, where these carbon fibrils are agglomerations of fibers whose diameters are within 3.5-70 nm, whose lengths are greater than about 100 times the diameters, the maximum diameter of the agglomeration of fibers is less than 0.25 mm, and the content of the fibrils whose agglomerated diameters fall within 0.10-0.25 mm is greater than 50%.

6. Oil-seal rubber compounds consisting of 100 weight parts of an oil resistant rubber and 1-30 weight parts of carbon fibrils, where these carbon fibrils are agglomerations of fibers whose diameters are within 3.5-70 nm, whose lengths are greater than about 100 times the diameters, the maximum diameter of the agglomeration of fibers is less than 0.25 mm, and the content of the fibrils whose agglomerated diameters fall within 0.10-0.25 mm is greater than 50%.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/01154

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. (5): H01B 1/00; C08K 3/04; B32B 9/00 U.S. Cl. 252/511; 524/495, 496; 428/367, 398, 408		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S. Cl.	252/511,510; 524/495,496,910,911,915; 260/Dig.17,Dig.15,Dig.21; 428/408,367,398,376	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>6</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X,Y	U.S. 4,663,230 05 MAY 1987 (TENNET) See column 3, para 1 with respect to Dimensions q the fibril material, column 7, para 4 for disclosure q matrix materials and the full disclosure for method q making, uses, other characteristics q the fibrils, etc.	1-6
A	U.S. 4,472,254 18 SEPTEMBER 1984 (HOUDAYER ET AL)	1-6
A	U.S. 4,654,475 31 MARCH 1987 (JACKSON ET AL)	1-6
A	U.S. 4,715,989 29 DECEMBER 1987 (SULLIVAN)	1-6
A P	U.S. 4,915,925 10 APRIL 1990 (CHUNG)	1-6
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>2</sup>
04 JUNE 1990		30 JUL 1990
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		 Josephine L. Barr

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